

## CLAIMS

1. A spherical annular seal member which is used particularly in an exhaust pipe spherical joint, comprising: a spherical annular base member defined by a cylindrical inner surface, a partially convex spherical surface, and large- and small-diameter-side annular end faces of said partially convex spherical surface; and an outer layer formed integrally with said partially convex spherical surface of said spherical annular base member, said spherical annular base member including a reinforcing member made from a compressed metal wire net and a heat-resistant material filling meshes of said metal wire net of said reinforcing member, compressed in such a manner as to be formed integrally with said reinforcing member in mixed form, and containing expanded graphite and an organic phosphorus compound, said outer layer including a heat-resistant material containing expanded graphite and an organic phosphorus compound, and a reinforcing member constituted by a metal wire net integrated with said heat-resistant material in mixed form, an outer surface of said partially convex spherical surface exposed to an outside in said outer layer being formed into a smooth surface in which said heat-resistant material and said reinforcing member are integrated in mixed form.

2. A spherical annular seal member which is used particularly in an exhaust pipe spherical joint, comprising: a spherical annular base member defined by a cylindrical inner surface, a partially convex spherical surface, and large- and small-diameter-side annular end faces of said partially convex spherical surface; and an outer layer formed integrally with said partially convex spherical surface of said spherical annular base member, said spherical annular base member including a reinforcing member made from a compressed metal wire net and a heat-resistant material filling meshes of said

metal wire net of said reinforcing member, compressed in such a manner as to be formed integrally with said reinforcing member in mixed form, and containing expanded graphite and an organic phosphorus compound, said outer layer including a lubricating composition constituted of at least boron nitride and at least one of alumina and silica, and a reinforcing member constituted by a metal wire net integrated with said lubricating composition in mixed form, an outer surface of said partially convex spherical surface exposed to an outside in said outer layer being formed into a smooth lubricating sliding surface in which said lubricating composition and said reinforcing member are integrated in mixed form.

3. A spherical annular seal member according to claim 2, wherein said lubricating composition contains 70 - 90 wt.% of boron nitride and 10 - 30 wt.% of at least one of alumina and silica.

4. A spherical annular seal member according to claim 2 or 3, wherein said lubricating composition further contains polytetrafluoroethylene resin.

5. A spherical annular seal member according to any one of claims 2 to 4, wherein said lubricating composition contains a mixture consisting of 70 - 90 wt. % of boron nitride and 10 - 30 wt. % of at least one of alumina and silica, and further contains not more than 200 parts by weight of polytetrafluoroethylene resin with respect to 100 parts by weight of said mixture.

6. A spherical annular seal member according to any one of claims 2 to 4, wherein said lubricating composition contains a mixture consisting of 70 - 90 wt. % of boron nitride and 10 - 30 wt. % of at least one of alumina and silica, and further contains 50 to 150 parts by weight of polytetrafluoroethylene resin with respect to 100 parts by weight of said mixture.

7. A spherical annular seal member according to any one of claims 1 to 6,

wherein said heat-resistant material containing said expanded graphite and said organic phosphorus compound of said spherical annular base member is exposed on said cylindrical inner surface.

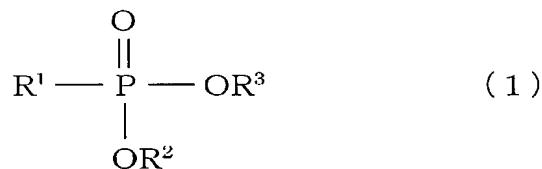
8. A spherical annular seal member according to any one of claims 1 to 7, wherein said reinforcing member constituted by said metal wire net of said spherical annular base member is exposed on said cylindrical inner surface.

9. A spherical annular seal member according to any one of claims 1 to 8, wherein said heat-resistant material containing said expanded graphite and said organic phosphorus compound of said spherical annular base member is exposed on at least one of said annular end faces.

10. A spherical annular seal member according to any one of claims 1 to 9, wherein said heat-resistant material contains 0.1 to 10.0 wt.% of said organic phosphorus compound and 90.0 to 99.9 wt.% of said expanded graphite.

11. A spherical annular seal member according to any one of claims 1 to 10, wherein said organic phosphorus compound is selected from the group consisting of an organic phosphonic acid or an ester thereof, an organic phosphinic acid or an ester thereof, a phosphoric ester, a phosphorous ester, and a hypophosphorous ester.

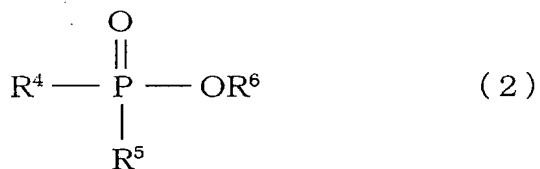
12. A spherical annular seal member according to claim 11, wherein the organic phosphonic acid or the ester thereof is represented by the following general formula (1):



wherein  $\text{R}^1$  is an alkyl group having a carbon number of 1 to 10, an aryl group

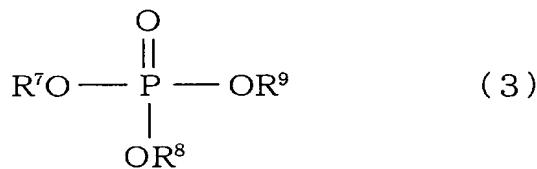
having a carbon number of 6 to 18, or an aralkyl group consisting of an alkylene portion having a carbon number of 1 to 10 and an aryl portion having a carbon number of 6 to 18, and each of R<sup>2</sup> and R<sup>3</sup> is a hydrogen atom, an alkyl group having a carbon number of 1 to 10, an aryl group having a carbon number of 6 to 18, or an aralkyl group consisting of an alkylene portion having a carbon number of 1 to 10 and an aryl portion having a carbon number of 6 to 18.

13. A spherical annular seal member according to claim 11, wherein the organic phosphonic acid or the ester thereof is represented by the following general formula (2):



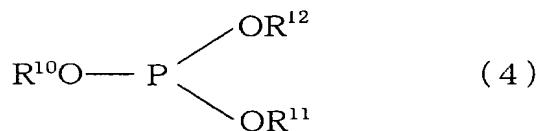
wherein R<sup>4</sup> is an alkyl group having a carbon number of 1 to 10, an aryl group having a carbon number of 6 to 18, or an aralkyl group consisting of an alkylene portion having a carbon number of 1 to 10 and an aryl portion having a carbon number of 6 to 18, and each of R<sup>5</sup> and R<sup>6</sup> is a hydrogen atom, an alkyl group having a carbon number of 1 to 10, an aryl group having a carbon number of 6 to 18, or an aralkyl group consisting of an alkylene portion having a carbon number of 1 to 10 and an aryl portion having a carbon number of 6 to 18.

14. A spherical annular seal member according to claim 11, wherein the phosphoric ester is represented by the following general formula (3):



wherein each of  $\text{R}^7$ ,  $\text{R}^8$ , and  $\text{R}^9$  is a hydrogen atom, an alkyl group having a carbon number of 1 to 10, an aryl group having a carbon number of 6 to 18, or an aralkyl group consisting of an alkylene portion having a carbon number of 1 to 10 and an aryl portion having a carbon number of 6 to 18, providing that a case where all of them are hydrogen atoms is excluded.

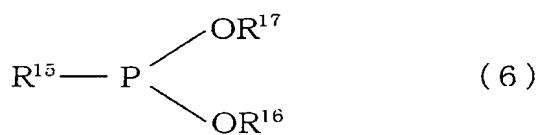
15. A spherical annular seal member according to claim 11, wherein the phosphorous ester is selected from a phosphorous triester which is represented by the following general formula (4) and a phosphorous diester or a phosphorous monoester which is represented by the following general formula (5):



wherein each of  $\text{R}^{10}$ ,  $\text{R}^{11}$ , and  $\text{R}^{12}$  is an alkyl group having a carbon number of 1 to 10, an aryl group having a carbon number of 6 to 18, or an aralkyl group consisting of an alkylene portion having a carbon number of 1 to 10 and an aryl portion having a carbon number of 6 to 18, and each of  $\text{R}^{13}$  and  $\text{R}^{14}$  is a hydrogen atom, an alkyl group

having a carbon number of 1 to 10, an aryl group having a carbon number of 6 to 18, or an aralkyl group consisting of an alkylene portion having a carbon number of 1 to 10 and an aryl portion having a carbon number of 6 to 18, providing that a case where both of  $R^{13}$  and  $R^{14}$  are hydrogen atoms is excluded.

16. A spherical annular seal member according to claim 11, wherein the hypophosphorous ester is a hypophosphorous diester (phosphonite) which is represented by the following general formula (6) or a hypophosphorous monoester which is represented by the following general formula (7):



wherein  $R^{15}$  is a hydrogen atom, an alkyl group having a carbon number of 1 to 10, an aryl group having a carbon number of 6 to 18, or an aralkyl group consisting of an alkylene portion having a carbon number of 1 to 10 and an aryl portion having a carbon number of 6 to 18, and each of  $R^{16}$ ,  $R^{17}$ , and  $R^{18}$  is an alkyl group having a carbon number of 1 to 10, an aryl group having a carbon number of 6 to 18, or an aralkyl group consisting of an alkylene portion having a carbon number of 1 to 10 and an aryl portion having a carbon number of 6 to 18.